PCT WORLD ORGANIZATION FOR INTELLECTUAL PROPERTY
International Office
INTERNATIONAL PATENT APPLICATION
PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification [6]: **A61K 7/06, 7/48**
(11) International Publication Number: **WO 98/14164 A2**
(43) International Publication Date: April 9, 1998 (4/9/98)
(21) International Application No.: PCT/EP97/05354
(22) International Filing Date: September 29, 1997 (9/29/97)

(30) Priority: 196 40 363.4 September 30, 1996 (9/30/96) Germany

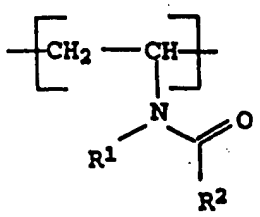
(71) Applicant (*for all contracting nations except the United States*): BASF AG (Germany / Germany), D-67056 Ludwigshafen (Germany)

(72) Inventor; and
(75) Inventor/ Applicant (*only for the United States*): Manfred Niessner (Germany / Germany), Gotenstrasse 25, D-67105 Schifferstadt (Germany); Claudia Nilz (Germany / Germany), Gartenstrasse 29, D-67127 Rödersheim Gronau (Germany); Peter Hössel (Germany / Germany), Birkenweg 10, D-67105 Schifferstadt (Germany); Stephan Kothrade (Germany / Germany), Albert Einstein Allee 17a, D-67117 Limburgerhof (Germany); Axel Sanner (Germany / Germany), Lorscher Ring 2c, D-67227 Frankenthal (Germany)

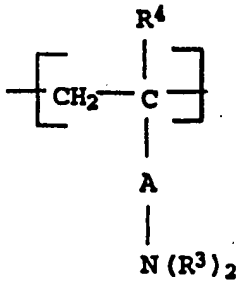
(74) Attorneys: Werner Kinzebach et al., Reltstötter, Kinzebach & Partners, Sternwartstrasse 4, D-81679 Munich (Germany)

(81) Contracting nations: Australia, Brazil, Canada, China, Czech Republic, Hungary, Israel, Japan, Korea, Mexico, Norway, Russian Federation, United States; European patent (Austria, Belgium, Switzerland, Germany, Denmark, Spain, Finland, France, Great Britain, Greece, Ireland, Italy, Luxemburg, Monaco, Netherlands, Portugal, Sweden).

Published
without the International Search Report; to be published again after receipt of the Search Report.



(I)



(II)

(54) Title: USE OF WATER-SOLUBLE COPOLYMERS AS ACTIVE INGREDIENTS IN COSMETICS

The present invention relates to the use of water-soluble copolymers consisting of such characteristic structural elements as a) acrylic acid amide of the general formula (I), where R^1 and R^2 stand, independently of each other, for H, alkyl, cycloalkyl, aryl or aralkyl, and b) units of the gneral formula (II), where A represents a chemical bond or an alkyl group, the R^3 residues stand, independently of each other, for H, alkyl, cycloalkyl, aryl, or arakyl, or, together with the nitrogen atom to which they are linked, an aromatic or non-aromatic five to seven member heterocyclic ring, possibly mono- or polysubstituted, possibly containing one or two more heteroatoms chosen from among O, N or S, and capable of being annelated with another aromatic or non-aromatic five to seven member ring, and R^4 represents H, alkyl or aralkyl. The invention also pertains to cosmetics containing said polymers.

USE OF WATER-SOLUBLE COPOLYMERS AS ACTIVE INGREDIENTS IN COSMETICS

Description

This invention relates to the use of water-soluble copolymers as ingredients in cosmetic preparations as well as the cosmetic preparations themselves containing these copolymers.

Polymers are used in a variety of ways in cosmetics and in medicine. In soaps, creams and lotions, for example, they are usually used as formulation aids, e.g., as thickeners, foam stabilizers or water absorbing agents or to reduce the irritating effect of other ingredients or to improve the dermal application of active ingredients. However, their function in cosmetics intended for use on hair is to influence the properties of hair. For example, conditioners are used to improve the dry and wet combability, the feel, sheen and appearance of the hair and also to impart antistatic properties to the hair. In addition, they may have a hair styling effect by forming a hydrophobic film on the hair.

Polymers with polar functionalities, often cationic functionalities having a greater affinity for the structurally induced negative surface charge of the hair are preferred. The structure and functioning of various hair treatment polymers are described in *Cosmetics & Toiletries*, vol. 103 (1988) 23. Commercial conditioner polymers include, for example, cationic hydroxyethyl cellulose, cationic polymers based in N-vinylpyrrolidone, acrylamide and diallyldimethyl ammonium chloride or silicones.

U.S. Patient 4,713,236 describes hair conditioners based on polymers containing vinylamine units, mentioning specifically polyvinylamine and the salts thereof, α-substituted polyvinylamines such as poly-(α-amino-acrylic acid) or copolymers which in addition to vinylamine also contain comonomers such as vinyl alcohol, acrylic acid, acrylamide, maleic anhydride, vinyl sulfonate and 2-acryl-amido-2-methylpropane-sulfonic acid polymerized into them. The possible applicability of copolymers with repeating vinylamine and vinyl carboxylic acid amide units as the active ingredient of a hair conditioner is not investigated in that document.

International Patent WO-A-96/03969 describes hair care products containing an N-vinyl-formamide homopolymer or a copolymer of N-vinyl-formamide units and another vinyl monomer selected from styrenes, alkyl esters of acrylic and methacrylic acid, vinyl esters with the formula CH_2=CH-OCO alkyl, N-alkyl-substituted acrylamides and methacrylamides, the esters of fumaric, itaconic and maleic acid, vinyl ethers, hydroxy-functionalized acrylates and meth acrylates, acrylamide, non-alkyl-substituted acrylamides and cyclic amides. Vinylpyrrolidone is mentioned as a specific example of a cyclic amide. Other examples of vinyl monomers include secondary, tertiary and quaternary amines such as dimethyldiallylammonium chloride, tert-butyl-aminoethyl methacrylate, dimethylaminoethyl methacrylate, diethylaminoethyl methacrylate [sic; in original twice], dimethylaminopropyl methacrylate and the quaternated derivatives thereof.

Japanese Patent 6,122,725 describes powdered vinyl-formamide homopolymers and copolymers. These polymers are used, for example, as an ingredient of toners, chromatography materials, carriers for immunodiagnostics and as fillers for dyes and cosmetics. However, this document does not describe these polymers as being suitable for use as conditioning agents, in particular as conditioners for shampoos.

Hydrolyzed oligomers of N-vinyl formamide are disclosed in U.S. Patent 5,373,076. Hypothetical applications for these polymers mentioned in that document include adhesives, binders, water treatment, paper production, petroleum and mineral production, medicine and body care.

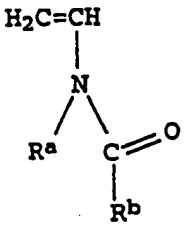
European Patent 510,246 and Japanese Patent 3,223,304 describe cross-linked homopolymers and copolymers of N-vinylcarboxylic acid amides, mainly in the anionic form, which are used as water absorbers and thickeners e.g., in the field of cosmetics.

Copolymers of acrylamide and (meth)acrylic acid which may also contain N-vinylcarboxylic acid amides as additional monomers are also used as thickeners in cosmetics or pharmaceutical preparations according to German Patent 34 27 220.

European Patent 452 758 describes hydrogen-rich gels for dermal cosmetic and medical applications containing a water-soluble polymer such as polyvinyl-formamide as an additional ingredient in addition to various surfactants.

Body care creams containing a monoaldehyde-modified vinylamine polymer are disclosed in U.S. Patent 5, 270, 379.

Copolymers that are used as hair setting agents, for example, and are composed of N-vinylamide monomers of the formula



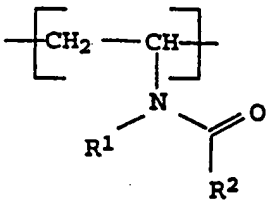
where R^a and R^b stand for H or C_1-C_5 alkyl and the monomer is selected from vinyl ethers, vinyl lactams, vinyl halides, vinyl esters of monobasic saturated carboxylic acids, (meth)acrylic acid esters, (meth)acrylic acid amides and nitriles and the esters, anhydrides and imides of maleic acid are described in German Patent 14 95 692.

British Patent 1,082,016 describes homopolymers of N-vinyl-N-methylacetamide and copolymers of these compounds with vinyl esters, vinyl ethers, (meth)acrylic acid esters, amides and nitriles, vinyl compounds derived from maleic and fumaric acid, styrene, butadiene and vinyl halides and their use in shampoo, hair set and hair spray formulations.

The object of the present invention is to make available new polymers with an improved efficacy in cosmetic preparations.

This object is achieved according to this invention by using water-soluble copolymers containing as the characteristic structural elements

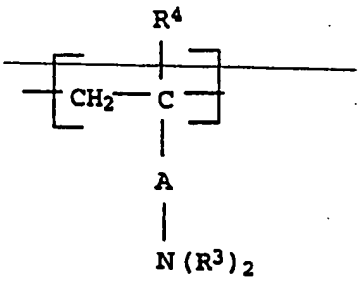
a) vinylcarboxylic acid amide units of general formula I



(I)

where
R^1 and R^2 independently of one another stand for H, alkyl, cycloalkyl, aryl or aralkyl, and

b) units of general formula II



(II)

where
A stands for a chemical bond or an alkylene group,

the R^3 groups independently of one another stand for H, alkyl, cycloalkyl, aryl or aralkyl, or together with the nitrogen to which they are attached they may also form a five- to seven-membered heterocyclic, aromatic or nonaromatic ring with one or more optional substituents and optionally containing one or two additional heteroatoms selected from O, N and S, where the heterocyclic ring may be anellated to another five- or six-membered aromatic or non-aromatic ring,

R^4 stands for H, alkyl or aralkyl

as well as the corresponding acid addition salts thereof,

as an ingredient in cosmetic preparations.

The copolymers used according to this invention preferably have a weight-average molecular weight in the range of approximately 10^3 to 10^8 g/mol, preferably approximately 10^4 to 10^7 g/mol.

Unless other information is given, the following definitions are applicable in the specific description of this invention:

Alkyl groups that can be used according to this invention include linear or branched saturated carbon chains with 1 to 12 carbon atoms. The following groups can be mentioned as examples: C_1-C_6 alkyl groups such as methyl, ethyl, N-propyl, isopropyl, N-butyl, sec-butyl, 2- or 3-methyl-pentyl and groups with a longer chain such as unbranched heptyl, octyl, nonyl, decyl, undecyl, lauryl and analogs thereof with one or more branches.

Alkaline groups that can be used according to this invention include linear C_1-C_{10} alkylene groups such as methylene, ethylene, propylene, butylene, pentylene and hexylene as well as branched C_1-C_{10} alkylene groups such as 1,1-dimethylbutylene, 1,3-dimethylbutylene, 1,1-dimethylbutylene, 1,2-dimethylpentylene and 1,3-dimethylhexylene. However, linear alkylene groups with 1 to 6 carbon atoms are preferred.

Cycloalkyl groups that can be used according to this invention include in particular C_3-C_{12} cycloalkyl groups such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclopropylmethyl, cyclopropylethyl, cyclopropylpropyl, cyclobutylmethyl, cyclobutylethyl, cyclopentylethyl, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl and the like.

Aralkyl groups that are suitable according to this invention include phenyl- and naphthyl-C_1-C_{12} alkyl groups, where the C_1-C_{12} alkyl part is defined as given above. Preferred aralkyl groups are phenyl C_1-C_6 alkyl groups.

Aryl groups that are suitable according to this invention include for example, phenyl and naphthyl.

Examples of five- to seven-membered N-heterocyclic groups include: five-membered groups such as pyrrolyl, pyrrolinyl, pyrrolidinyl; 1,2- and 1,3-oxazolyl, 1,2- and 1,3-thiazolyl; 1,2- and 1,3-oxazolinyl; 1,2- and 1,3-thiazolinyl; 1,2- and 1,3-oxazolidinyl; 1,2 and 1,3–thiazolidinyl; pyrazolyl, pyrazolinyl, pyrazolidinyl; imidazolyl, imidazolinyl, imidazolidinyl; 1,2,4-triazolyl, 1,3,4-triazolyl. Six-membered groups include pyridyl and piperidyl; pyridazinyl, pyrimidinyl, pyrazinyl; piperazinyl; 1,2-, 1,3- and 1,4-oxazinyl, morpholinyl, 1,2-, 1,3- and 1,4-thiazinyl; 1,2,3-, 1,2,4- and 1,3,4-triazinyl, 1,2,3-, 1,2,4- and

1,3,4-oxadiazinyl, 1,2,3-, 1,2,4- and 1,3,4-thiadiazinyl. Seven-membered groups include azepinyl, 1,2-, 1,3- and 1,4-diazepinyl, 1,2-, 1,3- and 1,4-oxazepinyl, 1,2-, 1,3- and 1,4-thiazepinyl.

Examples of anellated heterocyclic groups include indolyl, indazolyl, benzimidazolyl, benzoxazolyl, benzthiazolyl; quinolinyl, isoquinolinyl, 1,2-dihydroquinolinyl; phthalazinyl, quinazolinyl, quinoxalinyl; benzodiazepinyl, benzoxazepinyl and benzothiazepinyl.

The heterocyclic groups according to this invention may optionally have one or more substituents such as 1, 2 or 3 substituents, in particular 1 or 2 substituents. Suitable substituents are selected from alkyl, cycloalkyl, aryl, aralkyl, OH, O-alkyl, O-aryl, SH, S-alkyl, S-aryl, NH_2, NH-alkyl, NH-aryl, $N(alkyl)_2$, optionally in protonated form, $N\text{-}alkyl_3^+Z^-$, where Z stands for a group from an organic or inorganic acid such as COOH, CHO, COO-alkyl, $CONH_2$, CONH-alkyl, $CON(alkyl)_2$, CN and SO_3H where alkyl, cycloalkyl, aryl and aralkyl have the meanings given above.

Preferred copolymers contain as the characteristic structural elements vinylcarboxylic acid amide units of formula I where R^1 and R^2 independently of one another stand for H or an alkyl. R^1 especially preferably stands for H and R^2 stands for C_1-C_6 alkyl.

As the preferred units of formula II, copolymers according to this invention contain monomers in which A stands for a chemical bond or a C_1-C_6 alkyl group, in particular a chemical bond; R^4 stands for H or C_1-C_6 alkyl, in particular H; and the R^3 groups together with the nitrogen atom to which they are attached stand for a five- to seven-membered heterocyclic ring, optionally with one or more substituents according to the definition given above.

Preferred heterocyclic groups include five- or six-membered aromatic or non-aromatic rings which may optionally contain one other heteroatom selected from O, N and S, preferably N.

If the heterocyclic ring is substituted, it has one or two, preferably one additional substituent. Preferred substituents include C_1-C_6 alkyl, -OH, -O-C_1-C_6 alkyl, -O-phenyl, -SH, -S-C_1-C_6 alkyl, -S-phenyl, $-NH_2$, -NH-C_1-C_6 alkyl, -NH-phenyl, -N-(C_1-C_6 alkyl)$_2$, $-N(C_1\text{-}C_6\ alkyl)_3^+Z^-$, -COOH, -COO-$C_1$-$C_6$ alkyl, -$CONH_2$, -CONH-C_1-C_6 alkyl, $-CON(C_1\text{-}C_6\ alkyl)_2$, -CN and $-SO_3H$.

Preferred counterions Z^- include CL^-, Br^-, $H_2PO_4^-$, SO_4^{2-}, NO_3^-, $HCOO^-$, phenyl-SO_3^-. If the heterocyclic ring has a quaternated nitrogen heteroatom, then the counterion X^- has the meanings given for Z^-.

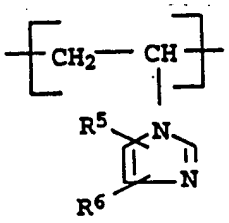
Preferred anellated heterocyclic rings include benzanellated heterocyclic rings.

Preferred examples of monomers of formula I include N-vinyl-formamide, N-vinyl-N-methyl-formamide, N-vinyl-N-ethyl-formamide, N-vinyl-N-propyl-formamide, N-vinyl-N-isopropyl-formamide, N-vinyl-N-butyl-formamide, N-vinyl-N-sec-butyl-formamide, N-vinyl-N-terephthalate butyl-formamide, N-vinyl-N-pentyl-formamide, N-vinylacetamide, N-vinyl-N-methyl-acetamide and N-vinyl-N-ethylacetamide.

Preferred examples of monomers of formula II include N-vinylpyrroles, N-vinylimidazoles, N-vinylimidazolines, N-vinylpyridines, N-vinylpyridazines, N-vinylpyrimidines, N-vinylpyrazines, N-vinylindoles, N-vinylindazoles and N-vinylbenzimidazoles, optionally with one or more substituents.

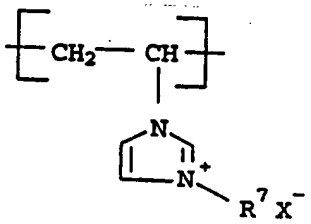
The heterocyclic functions are in the form of the free bases or they may be neutralized with mineral acids or organic acids or quaternated, in which case the quaternation is preferably performed with dimethyl sulfate, diethyl sulfate, methyl chloride or benyl chloride.

Especially preferred heterocyclic monomers are selected from imidazole and imidazolium monomers of the following formulas III and IV:



(III)

where
R^5 and R^6 independently of one another are selected from H, alkyl, aryl, aralkyl or together they may form a benzannellated ring



(IV)

where
X stands for a residue of an organic or inorganic acid and R^7 stands for H, alkyl or aralkyl and the corresponding imidazoline derivatives.

Especially preferred monomers of formula III are compounds in which R^5 and R^6 independently of one another stand for H or C_1-C_6 alkyl, especially H. Especially preferred monomers of formula IV are compounds in which R^7 stands for C_1-C_6 alkyl or X stands for Cl or Br.

Examples of imidazole and imidazoline monomers include N-vinyl-2-methylimidazole, N-vinyl-4-methylimidazole, N-vinyl-5-methylimidazole, N-vinyl-2-ethylimidazole, N-vinyl-N′-methyl-imidazolium chloride, N-vinyl-N′-ethyl-imidazolium chloride, N-vinyl-imidazoline, N-vinyl-2-methylimidazoline and N-vinyl-2-ethyl-imidazoline.

In addition, preferred copolymers also include those containing

a) 0.1 to 99.9 mol%, preferably 1 to 99, especially 5 to 95 mol% N-vinyl carboxylic acid amide units of formula I,

b) 0.1 to 99.9 mol%, preferably 1 to 99, especially 5 to 95 mol% units of formula II,

c) 0.1 to 99.8 mol%, preferably 0 to 98, especially 0 to 90 mol% monoethylenically unsaturated monomer units different from a) and b); and

d) 0 to 5 mol%, preferably 0 to 4, especially 0 to 3 mol% monomer units with at least two ethylenically unsaturated double bonds.

Examples of monomers c) include vinylamines and their salts, such as vinylammonium halides, vinyl alcohol, vinyl formate, vinyl acetate, vinyl propionate, vinyl butyrate, N-vinylpyrrolidone, N-vinyl caprolactam, N-vinyl ureas, C_1-C_6 vinyl ethers, monoethylenically unsaturated C_3-C_8 carboxylic acids and dicarboxylic acids as well as their esters, amides, anhydrides and nitriles, olefins and vinyl aromatics.

Suitable additional ethylenically unsaturated monomers c) include vinyl formate, vinyl acetate, vinyl propionate, vinyl butyrate, unsaturated C_3 to C_8 carboxylic acids such as acrylic acid, methacrylic acid, maleic acid, crotonic acid, itaconic acid and vinyl acetic acid as well as their alkali and alkaline earth metal salts, esters, amides and nitriles such as methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, propyl acrylate and butyl acrylate or glycol or polyglycol esters of ethylenically unsaturated carboxylic acids, where in each case only one OH group of the glycols and polyglycols is esterified e.g., hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxypropyl acrylate, hydroxypropyl methacrylate, hydroxybutyl acrylate, hydroxybutyl methacrylate or acrylic acid and methacrylic acid mono esters of polyalkylene glycols with a molecular weight from 1500 to 10,000. Also suitable are the esters of ethylenically unsaturated carboxylic acids with amino alcohols such as dimethylaminoethyl acrylate, dimethylaminoethyl methacrylate, diethylaminoethyl acrylate, diethylaminoethyl methacrylate, dimethylaminopropyl acrylate, dimethylaminopropyl methacrylate, diethylaminopropyl acrylate, diethylaminopropyl methacrylate, dimethylaminobutyl acrylate and diethylaminobutyl acrylate. The basic acrylates are in the form of the free bases, the salts with mineral acids such as hydrochloric acid, sulfuric acid and nitric acid, the salts of organic acids such as formic acid or benzenesulfonic acid or it may be in quaternated form.

Suitable quaternating agents include, for example, dimethyl sulfate, methyl chloride, ethyl chloride or benyl chloride.

In addition, other compounds that are suitable for use as monomer c) include unsaturated amides such as acrylamide, methacrylamide and N-alkyl mono- and di-amides with alkyl groups with 1 to 6 carbon atoms such as N-methylacrylamide, N,N-dimethylacrylamide, N-methyl-methacrylamide, N-ethylacrylamide, N-propylacrylamide and tert-butylacrylamide as well as basic (meth)acrylamides such as dimethylaminoethylacrylamide, dimethylaminoethyl-methacrylamide, dimethylaminoethyl-acrylamide, diethylaminoethyl-acrylamide, diethylaminoethyl-methacrylamide, dimethylaminopropyl-acrylamide, dimethylaminopropyl-methacrylamide, diethylaminopropyl-acrylamide and diethylaminopropyl-methacrylamide.

C_1-C_6 vinyl ethers such as vinyl methyl ether, vinyl ethyl ether, vinyl propyl ether, vinyl isopropyl ether, vinyl butyl ether, vinyl isobutyl ether, vinyl pentyl ether and vinyl hexyl ether may also be used as monomers c).

In addition, N-vinylpyrrolidone, N-vinylcaprolactam, N-vinyl urea and substituted N-vinyl ureas such as N-vinyl-N′-methyl urea and N-vinyl-N′-dimethyl urea may also be used as monomers c).

Monoethylenically unsaturated compounds with sulfa groups may also be used as monomers c), such as vinyl sulfonic acid, allyl sulfonic acid, methallyl sulfonic acid, styrene sulfonic acid or acrylic acid 3-sufloproplyl ester, methyacrylic acid 3-sulfopropyl ester and 2-acrylamido-2-methylpropane sulfonic acid.

The compounds having acid groups may be in the form of the free acids, the ammonium salts, the alkaline metal and alkaline earth metal salts.

Another modification of the copolymers can be achieved by having 0 to 5 mol% units of monomers d) with at least two ethylenically unsaturated unconjugated double bonds also polymerized into the copolymers. Such comonomers are generally used as crosslinking agents in copolymerization. Use of these comonomers during copolymerization causes an increase in the molecular weight of the copolymer. Suitable compounds of this type include, for example, methylenebisacrylamide, esters of acrylic acid and methacrylic acid with polyhydric alcohols such as glycol diacrylate, glycerin triacrylate, glycol dimethacrylate, glycerin trimethacrylate as well as polyols esterified at least twice with acrylic acid or methacrylic acid such as pentaerythritol and glucose. Suitable crosslinking agents also include divinylbenzene, divinyldioxane, pentaerythritol triallyl ether, pentaallyl sucrose, divinylurea and divinylethylene urea.

The copolymers to be used according to this invention are obtained by methods known in the literature by copolymerization of monomers of formulas I (monomers a)) and formulas II (monomers b)) initiated by free radicals, optionally in the presence of the above-mentioned additional monomers c) and/or d) and optionally then partially splitting off the carbonyl group by hydrolysis. Suitable synthesis methods are described, for example, in European Patent 71,050 A, European Patent 251,182 A and European Patent 216,387 A to which reference is herewith made explicitly.

The polymerization may be carried out in the presence or absence of an inert solvent or diluent. Since polymerization carried out in the absence of inert solvents or diluents usually leads to heterogeneous polymer products, polymerization in an inert solvent or diluent is preferred. For example, suitable inert solvents include those in which the open-chain N-vinylcarboxylic acid amides are soluble. For example, inert solvents such as methanol, ethanol, isopropanol, n-propanol, n-butanol, tetrahydrofuran, dioxane, water and mixtures of the above-mentioned inert solvents are suitable for solution polymerization. Polymerization may be carried out continuously or discontinuously. It takes place in the presence of initiators which form free radicals and are used in amounts of 0.01 to 20 wt%, preferably 0.05 to 10 wt%, based on the monomers. The polymerization may optionally also be initiated easily under the influence of high-energy radiation such as electron beams or UV rays.

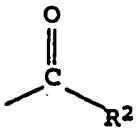
To produce polymer products with a low molecular weight, e.g., from 1000 to 100,000, preferably 5000 to 50, 000, the polymerization is preferably carried out in the presence of regulators. Suitable regulators include, for example, organic compounds containing sulfur in a bound form, including mercapto compounds such as mercaptoethanol, mercaptopropanol, mercaptobutanol, mercaptoacetic acid, mercaptopropionic acid, butylmercaptan, dodecylmercaptan. Suitable regulators also include allyl compounds such as allyl alcohol, aldehydes such as formaldehyde, acetaldehyde, propionaldehyde, n-butyraldehyde and isobutyraldehyde, formic acid, ammonium formate, propionic acid, hydrazine sulfate and butanols.

If the polymerization is carried out in the presence of regulators, 0.05% to 20 wt% is needed, based on the monomers used in polymerization. The monomers are generally polymerized in an inert gas atmosphere from which atmospheric oxygen is excluded. During the polymerization, a good mixing of the reactants is generally ensured. In the case of smaller batches where reliable dissipation of the heat of polymerization is guaranteed, the monomers may be polymerized discontinuously by heating the reaction mixture to the polymerization temperature and then allowing the reaction to take place. These

temperatures are in the range of 40 to 180°C, in which case it is possible to work under normal pressure, a reduced pressure or an elevated pressure. Polymers with a high molecular weight are obtained by performing the polymerization in water. For example, to produce water-soluble polymers in an aqueous solution, this may be carried out in an aqueous solution, as a water-in-oil emulsion or by the method of inverse suspension polymerization.

To prevent saponification of the monomeric N-vinyl carboxylic acid amides during polymerization in an aqueous solution, the polymerization is preferably performed in a pH range of 4 to 9, especially 5 to 8. In many cases it is advisable to also work in the presence of buffers such as primary or secondary sodium phosphate.

Copolymers that can be used according to this invention and contain as monomer c) a vinylamine or its corresponding ammonium compound are obtained from the polymer products described above, optionally by partial cleavage of the group



from the N-vinyl carboxylic acid amide units, forming amine groups or ammonium groups. The hydrolysis is preferably performed in water under the influence of acids, bases or enzymes, but it may also be carried out in the absence of the above-mentioned hydrolysis agents. Different degrees of hydrolysis are obtained, depending on the reaction conditions in hydrolysis, i.e., the amount of acid or base, based on the polymer to be hydrolyzed, and also depending on the reaction time and temperature. Hydrolysis is continued until 0.1 to 99.9 mol%, preferably 1 to 99 mol% and especially 5 to 95 mol% of the carboxylic acid amide residues have been split off by hydrolysis.

Acids suitable for performing this hydrolysis include, for example, mineral acids such as hydrogen halide (gaseous or in aqueous solution), sulfuric acid, nitric acid, phosphoric acid (ortho-, meta- or polyphosphoric acid) or organic acids such as C_1 to C_5 carboxylic acids such as formic acid, acetic acid or propionic acid or aliphatic and aromatic sulfonic acids such as methane sulfonic acid, benzene sulfonic acid or toluene sulfonic acid. In hydrolysis with acids, the pH is 0 to 5. Per carboxylic acid group to be split off in the polymer, 0.05 to 1.5 equivalents of acid are needed, preferably 0.4 to 1.2 eq.

In hydrolysis with bases, metal hydroxides of metals of the first and second main groups of the periodic system may be used e.g., lithium hydroxide, sodium hydroxide, potassium hydroxide, calcium hydroxide, strontium hydroxide and barium hydroxide. However, ammonia or alkyl derivatives of ammonia such as alkylamine or arylamines such as triethylamine, monoethanolamine, diethanolamine, triethanolamine, morpholine, piperidine, pyrrolidine or aniline are also suitable. In hydrolysis with bases, the pH is 8 to 14. The bases may be used in a solid, liquid or optionally even gaseous state, diluted or undiluted. Ammonia, sodium hydroxide or potassium hydroxide is preferred. Hydrolysis in the acidic or alkaline pH range takes place at temperatures of 20 to 170°C, preferably 50 to 120°C. It is also concluded after about 2 to 8 hours, preferably 3 to 5 hours.

A procedure in which the acids or bases are added in aqueous solution has proven especially suitable. After hydrolysis, neutralization is generally performed so that the pH of the hydrolyzed polymer solution is 2 to 8, preferably 3 to 7. Neutralization is necessary when progress of the hydrolysis of partially hydrolyzed polymers is to be avoided or delayed. The hydrolysis may also be performed with the help of enzymes.

Optionally another modification of the polymers occurs in hydrolysis of copolymers containing N-vinylcarboxylic acid amide units to the extent that the comonomers polymerized into them also undergo hydrolysis. This results, for example, in vinyl alcohol units from polymerized units of vinyl esters. Depending on the hydrolysis conditions, the polymerized vinyl esters may be partially or completely saponified.

In partial hydrolysis of copolymers containing vinyl acetate units, the hydrolyzed copolymer includes in addition to unchanged vinyl acetate units also vinyl alcohol units and N-vinyl carboxylic acid amide units and vinylamine units. Units of monoethylenically unsaturated carboxylic acid anhydrides, esters and amides form carboxylic acid units in hydrolysis. Polymerized monoethylenically unsaturated carboxylic acids themselves are not changed in hydrolysis. Carboxylic acid amide units and carboxylic acid units may also be formed from polymerized monoethylenically unsaturated nitriles. The degree of hydrolysis of the copolymerized comonomers can also be determined easily by analysis.

The amine functions may be used in the form of the free bases or in salt form neutralized with mineral acids or organic acids such as formic acid, acetic acid, valeric acid, 2-ethylhexanoic acid, lauric acid, adipic acid, benzoic acid, p-methoxybenzoic acid, lactic acid, citric acid. In addition, there is also the possibility of alkylating or quaternating the unsubstituted amine groups. The alkylation and quaternation are performed with the help of conventional alkylating agents such as alkyl halides e.g., methyl chloride, methyl bromide, methyl iodide, ethyl bromide, ethyl iodide or benzyl bromide or dimethyl sulfate or diethyl sulfate. The reaction may be carried out in an aqueous medium, in inert organic solvents or in mixtures of water with solvents, optionally with phase transfer catalysis. The alkylation and quaternation are preferably performed in an aqueous medium.

The copolymers used according to this invention have a molecular weight of 1000 to 10,000,000, preferably 10,000 to 5,000,000, which corresponds to a K value of approximately 5 to 300 or 10 to 250, measured on 1% aqueous solutions at a pH of 7 and a temperature of 25°C according to H. Fikentscher, *Cellulose-Chemie* [Cellulose Chemistry], vol. 13, pp. 58 to 64 and 71 to 74 (1932).

The copolymers described above are used as active ingredients in cosmetic preparations, e.g., as conditioners for shampoo, hair lotions, emulsions, rinses, gels, foams and pretreatment and aftertreatment products for dyeing hair and permanent waves as well as hair setting and styling products with hair care properties. In addition, they may be used as thickeners in cosmetic formulations and in cosmetic preparations for oral care.

It has surprisingly been found that the N-vinyl-formamide copolymers according to this invention have improved properties in cosmetic formulations. These improvements in properties are most notable in shampoo formulations. The copolymers according to this invention are preferably used in conventional shampoo formulations with sodium and ammonium lauryl ether sulfate as the basic surfactant and optionally additional cosurfactants such as alkyl, polyglycosides, cocamido propylbetaines, sulfosuccinic acid esters, sec-alkane sulfonates, α-olefin sulfonates, protein fatty acid condensates, N-acyl

sarcocinates, taurides, methyl taurides, fatty acid ethionates, N-acyl glutamates, ether carboxylic acid derivatives, alkyl phospate esters, alkyl phosphate esters [sic, duplication] alkyl phosphate esters, alkyl betaines, alkyl amidopropylbetaines, sulfobetaines, alkyl glyceryl ether sulfonates, cocoamphocarboxyglycinates and sorbitan derivatives. After using the N-vinyl-formamide copolymers in the above-mentioned shampoos, the wet combability of the hair is improved in particular. Furthermore, sheen, volume and body and excellent strength are imparted to the hair. The shampoos thus have a washing effect, a conditioning effect and a setting effect (3-in-1 shampoos) and the polymers are effective even when used in small amounts.

The copolymers according to this invention also have good conditioning and strengthening effects in hair lotions, emulsions, rinses and styling products such as gels and foams and in pretreatment and aftertreatment products for hair dye and permanent waves, where they have excellent hair care properties.

In addition, these copolymers may also be used as conditioners and thickeners in skin care products such as creams, ointments, emulsions and lotions and for oral care in toothpastes, gels and mouthwash.

This invention therefore also concerns cosmetic agents containing at least one polymer according to the above definition in a cosmetic vehicle and optionally in combination with other cosmetic active ingredients.

The polymer products according to this invention are usually present in the cosmetic agents in an amount of about 0.01 to 15 wt% such as approximately 0.1 to 10 wt%, based on the total weight of the agent. In addition to the conventional cosmetic vehicles, these products may also contain other conventional additives such as surface-active agents, thickeners, geling agents, solubilizers, humectants, binders, propellants, polymers such as silicones, sequestering agents, chelating agents, viscosity modifiers, opacifiers, stabilizers, pearlizing agents, dyes, perfumes, organic solvents, preservatives, pH-adjusting agents and optionally other conditioners may also be present.

This invention will now be illustrated in greater detail on the basis of the following examples which do not limit the scope in any way.

Synthesis example

Synthesis of a copolymer of 90 mol% N-vinyl-formamide and 10 mol% N-vinyl-N′-methylimidazolium chloride (copolymer 1).

A mixture of 180 g N-vinyl-formamide, 44.4 g of a 45% aqueous solution of N-vinyl-N′-methylimidazolium chloride and 775.6 g water was heated to 70° under nitrogen in a laboratory apparatus with a reflux condenser and an anchor mixer. After adding a solution of 0.6 g 2,2′-azobis(2-amidinopropane) dihydrochloride in 10 mL water, a temperature of 70°C was maintained for 8 hours while stirring. The pH was prevented from dropping below a level of 7 by adding ammonia during polymerization. After cooling the reaction mixture, a clear colorless polymer solution with a solids content of 20.1% was obtained. The K value of the polymer was 104(measured on a 0.1% solution in 5% saline solution) . Determination of the K value is described by H. Fikentscher, "System of Celluloses Based on Their Viscosity in Solution," *Cellulose-Chemie*, vol. 13, (1932), pp. 58-64 and 71-74.

Application example

Copolymer 1 according to the synthesis example was compared with the known copolymers 2 and 3 with regard to its hair conditioning effect.

Copolymer 2 (state of the art)

Conventional commercial copolymer of acrylamide and diallyldimethylammonium chloride with a molecular weight of about 1,000,000 (Merquat S from Merck Calgon).

Copolymer 3 (state of the art)

Conventional commercial cationic hydroxyethyl cellulose (Celquat H 100 from National Starch & Chem. Invention. Hold. Corp.).

To test this product as a conditioner for shampoo, these copolymers 1 to 3 were added in the stated amount to a standard test shampoo containing 15.0 wt% sodium lauryl ether sulfate with two to three ethylene oxide units (Texapon NSO from Henkel KG). On the basis of defined hair tresses the influence of the polymers on wet combability was tested. To do so the hair tresses are washed with the test shampoo containing the polymer and then rinsed and the combing force was measured. A hair tress treated with test shampoo without an additive was used as the blank sample. The results are summarized in Table 1.

Table 1:

Copolymer	Amount added (% by weight)	Decrease in combing force (against blank value)
1	0.1	43
2	0.1	5
	1.0	18
3	0.1	25

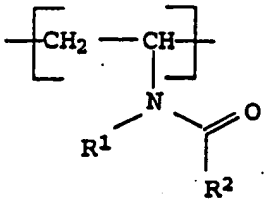
The reduction in combing force is calculated according to the following formula:

$$\text{reduction (\%)} = [\,(\text{measured value} \times 100) / (\text{blank value})\,] - 100$$

Thus a great reduction in combing force is to be evaluated as positive.

Patent Claims

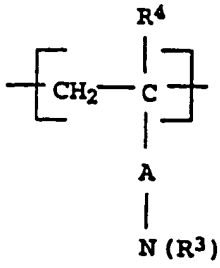
1. Use of a water-soluble copolymer containing as the characteristic structural elements
   a) vinyl carboxylic acid amide units of general formula I



(I)

where
R^1 and R^2 independently of one another stand for H, alkyl, cycloalkyl, aryl or aralkyl, and

   b) units of general formula II



(II)

where
A stands for a chemical bond or an alkylene group,

the R^3 groups, independently of one another, stand for H, alkyl, cycloalkyl, aryl or aralkyl, or together with the nitrogen to which they are attached, they may also form a five- to seven-membered heterocyclic, aromatic or nonaromatic ring with one or more optional substituents and optionally containing one or two additional heteroatoms selected from O, N and S, where the heterocyclic ring may be anellated to another five- or six-membered aromatic or non-aromatic ring,

R^4 stands for H, alkyl or aralkyl

as well as the corresponding acid addition salts thereof,

as an ingredient for use in cosmetic preparations.

2. Use according to Claim 1, characterized in that the copolymer includes units of formula II, where A and R^4 have the meanings given above, and the R^3 groups together with the nitrogen atom to which they are attached stand for a five- to seven-membered heterocyclic, aromatic or non-

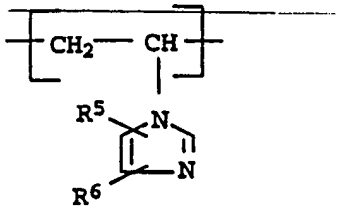
aromatic ring, which optionally has one or more substituents and optionally contains one or two other heteroatoms selected from O, N and S, where the heterocyclic ring may be anellated with another five- or six-membered aromatic or non-aromatic ring, and where the heterocycle may also be in protonated or quaternated form.

3. Use according to Claim 1 or 2, characterized in that the copolymer has a weight-average molecular weight in the range of approximately 10^3 to 10^8 g/mol.

4. Use according to one of the preceding claims, characterized in that the copolymer contains
   a) 0.1 to 99.9 mol% N-vinyl carboxylic acid amide units of formula I,
   b) 0.1 to 99.9 mol% units of formula II,
   c) 0.1 to 99.8 mol% monoethylenically unsaturated monomer units different from a) and b); and
   d) 0 to 5 mol% monomer units with at least two ethylenically unsaturated double bonds.

5. Use according to Claim 4, characterized in that the monomer units c) are derived from vinyl alcohol, vinyl formate, vinyl acetate, vinyl propionate, vinyl butyrate, N-vinyl-pyrrolidone, N-vinyl caprolactam, N-vinyl ureas, C_1-C_6 vinyl ethers, monoethylenically unsaturated C_3-C_8 carboxylic acids and dicarboxylic acids as well as their esters, amides, anhydrides and nitriles, olefins, vinyl aromatics, vinylamines, vinylammonium halides and monomers containing sulfonic acid groups with a polymerizable double bond.

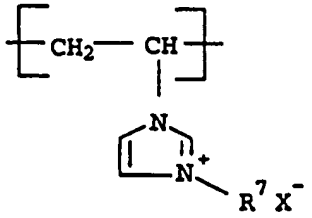
6. Use according to one of the preceding claims, characterized in that the units b) are selected from
   i)



(III)

where
R^5 and R^6 independently of one another are selected from H, alkyl, aryl, aralkyl or together they may form a benzanellated ring; and

ii)



(IV)

where
X stands for a moiety of an organic or inorganic acid, and R^7 stands for H, alkyl or aralkyl.

7. Use of a copolymer according to one of Claims 1 through 6 as a conditioner or thickener.

8. Use according to one of the preceding claims, characterized in that the cosmetic preparation is selected from hair cosmetic preparations, skin care preparations and mouth care preparations.

9. Use according to Claim 8 in hair setting agents, hair treatment solutions, lotions, emulsions, rinses, gels, foams, pretreatment and aftertreatment products for hair dyeing and permanent waves, hair styling agents with care properties or shampoos.

10. Use according to Claim 9 as a conditioner for shampoo.

11. Cosmetic preparation containing at least one polymer according to one of Claims 1 through 6 in a cosmetic vehicle and optionally in combination with other active cosmetic ingredients.